

Some Factors Influencing Crystal Habit

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SOME FACTORS INFLUENCING CRYSTAL HABIT*

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ABSTRACT

The influences of the following factors on crystal habit were investigated:

1. Temperature of pure aqueous solutions.
2. Presence of inorganic compounds in solution.
3. Presence of organic compounds in solution.
4. Presence of thickening substances.
5. Presence of suspensions.

Crystals were grown under temperature conditions varying from 5°C to 30°C. At a slow rate of crystal growth, the crystals of the salts investigated (barium nitrate, strontium nitrate, and lead nitrate) are of very simple habit when grown at low temperatures (5°C to 10°C), and become increasingly more complex with increase in temperature.

The presence of impurities in solutions was found to exert an influence on crystal habit. A number of anhydrous nitrates varying appreciably in solubility were employed to serve as inorganic impurities. An inorganic impurity of greater solubility than the salt crystallizing has the effect of producing crystals of simpler habit than those formed from a pure aqueous solution under similar temperature conditions and about the same rate of crystal growth. If, however, the salt present as an impurity is less soluble than the salt crystallizing from solution the crystals formed are more complex in habit.

The crystal habit was likewise influenced materially by the presence of organic substances added as impurities. The results in general suggest that the effect of some impurities, inorganic and organic, is due in part to the influence of the impurity upon the property of the water acting as the solvent. The influence of impurities on crystal habit is not always due to adsorption of the impurity by the crystal faces nor to the regular inclusion of the impurity by the crystal.

INTRODUCTION

HISTORICAL

One of the most interesting phenomena associated with the study of crystals is that of crystal habit. It is rather surprising to find that there has been very little intensive systematic study devoted to this fascinating subject. Investigators for some reason have not devoted much time and energy to solve the mysteries of

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crystal development. The subjects of definite polyhedral form, symmetry, and crystal structure have issued a stronger challenge.

It is a matter of general observation that there are a large number of minerals, each represented by several different crystal forms. Furthermore, these forms or combination of forms for any one mineral may vary considerably in relative size. These observations are most pronounced in the case of the more commonly occurring minerals. Calcite and pyrite, for example, are exceedingly common minerals represented by very pronounced difference in crystal forms and combination of forms. Good crystals illustrating this may be found in all museums exhibiting minerals, and full descriptions with drawings and photographs may be seen in any standard text on mineralogy.

Crystal habit in this paper is here considered to mean the crystal form, or any manner of combination of forms, by which a mineral, or any other crystalline substance, may be represented. Distortions, although often characteristic, as for example in the case of many quartz crystals, are not to be considered in this discussion under the term *habit*.

The terms dominant and predominant are used quite frequently in describing experimental results. The term dominant is applied to the form in combination which is relatively the larger or largest in size. The term predominant refers to the habit among a group of crystals that occurs more often than any other in that group.

To a crystallographer it is of extreme interest to know the factors that cause a substance, of definite chemical composition possessing in crystalline state well defined elements of symmetry and a definite crystal structure, to vary in crystal habit. It is the purpose of this paper to report some of the results obtained from a large number of experiments that have been conducted with the object of determining some of the factors that influence crystal habit.

In recent years, particularly, a number of investigators have been interested in the study of crystal habit. Apparently, the greatest amount of effort has been directed towards a study of the effect of foreign substances. Reports have been published quite widely dealing in some way with the effect of foreign substances on crystal habit.

Boydant¹ and several others have tried to determine why the presence of a foreign substance can produce an influence so as to

¹ Boydant: Report of Smithsonian Institution, 1908-09, p. 272.

modify crystal habit. However, their efforts to determine the exact nature of the influence have not been very successful. One reason quite generally advanced, credited to H. Marc,² is that the foreign substance is adsorbed by the crystal faces. Since the properties of the crystal faces of different forms vary, the amount of adsorption by these faces may likewise vary. This retards the development of certain forms producing crystals of different habit. Wherry³ suggests that in the case of crystals highly modified the effect is produced not only by one adsorbable impurity but by several.

P. Curie⁴ developed a very elaborate theory referred to sometimes as the "attractive theory." Curie sets forth with detailed mathematical calculations the idea that capillary action exists between the liquid and the crystal, and that this effect varies with the nature of the crystal face and the nature of the liquid. According to Curie the faces which develop require a minimum expenditure of capillary energy and that, therefore, the dominant forms are those whose constant capillarity is the least, and that since foreign substances influence the capillary constant, they, therefore, influence crystal habit.

Another explanation quite generally met with, as one searches the literature bearing on crystal habit, is that the foreign substance is taken into the crystal from solution through simultaneous crystallization and is distributed in some orderly fashion. By virtue of this, the impurity modifies or influences the crystal habit. Paul Gaubert⁵ vigorously supports this idea and has reported somewhat at length on experiments using different dyes as foreign substances in solution to supply evidence in support of his view.

METHOD FOR GROWING CRYSTALS

For the purpose of growing crystals a combination of the following crystallizing dishes was used:

- No. 1. 50 mm. diameter, 55 mm. deep.
- No. 2. 70 mm. diameter, 50 mm. deep.
- No. 3. 150 mm. diameter, 75 mm. deep.

² J. W. Mellor: A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. 1, p. 630.

³ Edgar T. Wherry. At the Surface of a Crystal. *Am. Mineral.*, 9, No. 3, p. 53.

⁴ Report of Smithsonian Institution, 1908-09, p. 272.

⁵ Paul Gaubert: *Revue Scientifique, Paris*, 41, No. 3, Jan. 15, 1910.

Each set up consisted of three dishes of No. 1 each containing the solution of the salt under consideration. These three dishes and one No. 2 dish containing concentrated sulphuric acid were covered by dish No. 3.

Solutions were made with distilled water and for most purposes 25 cc. of solution were placed in each dish. The majority of the experiments were carried on with three such sets of dishes for one experiment. It was highly desirable to make observations of crystals while they were growing in the mother liquor. In order to make observations for record on crystals grown from solutions which had not been disturbed, three sets of experiments, under the same conditions, were conducted simultaneously.

The dishes were placed on felt cloth which in turn was securely tacked to a wooden bench or wooden table top. The felt served as an insulation and also to reduce the effect of vibrations somewhat. The quantity of salt used in making up solutions was weighed carefully and the desired concentration was determined with the aid of solubility tables.

Temperature conditions in the room and in connection with any special experiments were determined by means of maximum and minimum thermometers. The experiments from which results were obtained for record were conducted under conditions where the temperature was controlled to within $\pm 2.5^{\circ}\text{C}$.

Methods for growing crystals with the temperatures controlled by thermostats were considered for this work. While schemes such as described by Hostetter⁶ and others are most excellent for obtaining homogeneous crystals of fairly large size, they could not be used to advantage for the work undertaken.

Observations were made on crystals during the period of crystal growth, while the crystals were still in the mother liquor. Crystals were also carefully observed after being removed from the mother liquor. All observations were made with a 20 power Leitz binocular microscope. A special arrangement of lights was adapted so that crystals could be observed by reflected light or by transmitted light or by both simultaneously.

⁶ J. C. Hostetter: *J. Wash. Acad. Science*, 9, No. 4, pp. 85-94.

EXPERIMENTAL DATA

RATE OF CRYSTAL GROWTH

Since the rate of crystal growth will vary with the rate of evaporation, it follows that if the rate of evaporation is controlled so that it is fairly constant, the rate of crystal growth will also be fairly constant.

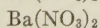
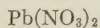
Four methods were used to vary the rate of evaporation:

- (1) A continuous partial vacuum was created by connecting a suction pump to a dessicator containing crystallizing dishes No. 1.
- (2) Three crystallizing dishes, No. 1, containing the solutions, were placed under the large dish No. 3. Under this same dish was also placed dish No. 2 with some concentrated sulphuric acid. This arrangement allows a comparatively uniform rate of evaporation.
- (3) Dish No. 1 was covered first with filter paper, then with a glass plate placed immediately on top of the filter paper and finally a weight of at least 250 grams was placed on the glass plate. This arrangement was placed under dish No. 3. The filter paper absorbs some of the water vapor and consequently allows some evaporation to go on. However, the rate is much slower than in (2).
- (4) A rubber stopper was tightly fitted to crystallizing dish No. 1. This prevented evaporation entirely.

The rate of crystal growth may also be influenced by rate of cooling. In general the solubility of a substance increases with the temperature of the solvent and this is true of all the salts used in these experiments.

SALTS USED IN THE EXPERIMENTS

The results reported in this paper were obtained largely from observations made upon the following three salts:



These three salts crystallize in the cubic system, in the tetrahedral pentagonal dodecahedral class of symmetry. Good crystals may be grown with very little difficulty, and for work dealing with crystal habit it is very important that the crystals obtained be sufficiently free from distortion to permit easy recognition and large enough so that the forms may be determined with the aid of a 20 power binocular microscope.

Other salts also were used in this study and crystals were grown of the following: NaCl, NaNO₃, NaBrO₃, NaClO₃, KI, KF, NaI, NaF, NaBr, and LiCl. The results were noted and were considered in connection with those of the three salts first mentioned, in arriving at interpretations.

Crystal growth was obtained by evaporation at fairly constant temperatures. The rate of evaporation was varied for different experiments. For most of the experiments two rates of evaporation were considered and for a few three rates. The rate of evaporation obtained by producing a partial vacuum with a suction pump will be referred to as "fast." The rate obtained under dish No. 3 in the presence of concentrated sulphuric acid will be referred to as "medium." The rate obtained under dish No. 3 by placing filter paper over the evaporating dish will be referred to as "slow." Experiments carried on with a rubber stopper tightly fitting the evaporating dish are regarded as "no evaporation."

The temperatures used were mainly the following:

5°C to 10°C
15°C to 20°C
20°C to 24°C
25°C to 30°C

The terms "medium" and "slow" refer to the method rather than to the actual rate of evaporation or of crystal growth. Experiments are reported, for instance, as evaporation "medium" with temperature conditions 15°C to 20°C. Experiments are also reported as evaporation "medium" with temperature conditions 20°C to 24°C. The scheme for allowing evaporation to take place is the same in each case. The actual rate must be somewhat different because there is a difference in temperature.

For highly quantitative work of a limited scope of this subject it would undoubtedly be important to define rate of crystal growth in terms of the actual increase in volume and the increase in the total surface area. This work, however, is in the nature of a preliminary report in this field and is approached from a fairly broad point of view. A quantitative consideration of rate of crystal growth, therefore, has for the present purpose of this work been omitted.

Experiments under the above conditions of evaporation and temperature were carried on (A) with pure aqueous solutions of the salts, and (B) with solutions containing impurities. The

impurities considered were a set of inorganic salts, organic compounds, viscous liquids and suspensions.

A. CRYSTALS FROM PURE AQUEOUS SOLUTIONS

EVAPORATION "FAST"—TEMPERATURE 20°C–24°C

In each of three dishes was placed the following solution:

35 cc. H_2O
24 gm. $\text{Pb}(\text{NO}_3)_2$

At the time the experiment was started there were from 25 to 50 small crystals in the liquor in each dish. The three dishes were placed in a dessicator and the dessicator connected to a suction pump. The crystals in one dish were examined after 12 hours and in the remaining two after 36 hours.

All the crystals in the liquor were combinations of $\pm$ tetrahedrons about equally developed. The crystals resembled slightly tabular octahadrons. All were milky and opaque. The above experiment was repeated with solutions of barium nitrate and strontium nitrate with the result that the crystals obtained in each case were all of the same habit as those obtained with lead nitrate. The crystals of barium nitrate were considerably smaller than those of lead nitrate or of strontium nitrate. The barium nitrate crystals were clear and transparent.

EVAPORATION "MEDIUM"—TEMPERATURE 5°C–10°C

In each of three dishes was placed the following solution:

25 cc. H_2O
2.2 gm. $\text{Ba}(\text{NO}_3)_2$

At the end of 12 hours of crystal growth the crystals of barium nitrate obtained were single tetrahedrons. The crystals were examined while in the liquor and a very interesting feature was noticed. The second tetrahedron could be seen to develop slowly while the crystals were being observed. The increase in temperature was not rapid enough to cause a solvent action to take place and produce a rounding of the edges and corners. The temperature in the room at the time of this experiment was but slightly higher than that of the interior of the box in which the experiments were set up. However, there was some heating effect from the light used for observation and the change in habit is explained as caused by this slight change in temperature. Crystal growth had not proceeded far enough to have reached a state of equilibrium. Because

evaporation was taking place, the process of crystal growth continued even with a slight increase in temperature of the solution.

After 36 hours the crystals in the two remaining dishes were single tetrahedrons and combinations of $\pm$ tetrahedrons with a predominance of single tetrahedrons. Of the combinations one form was dominant. The maximum thermometer indicated that the temperature for a short period had been in the neighborhood of 10°C . During the first 12 hours it had not been above 7°C . The increase in temperature may account for the variation in habit.

EVAPORATION "MEDIUM"—TEMPERATURE 15°C – 20°C

25 cc. H_2O

17 gm. $\text{Pb}(\text{NO}_3)_2$

Results after 12 hours of crystal growth showed a predominance of crystals with $\pm$ tetrahedrons in combination of equal development. A minority of the crystals were combinations of $\pm$ tetrahedrons with one form decidedly dominant. After 36 hours and 60 hours the predominance of $\pm$ tetrahedrons of equal development had successively increased.

EVAPORATION "MEDIUM"—TEMPERATURE 12°C – 20°C

25 cc. H_2O

2.2 gm. $\text{Ba}(\text{NO}_3)_2$

After 12 hours of crystal growth all the crystals of barium nitrate were combinations of $\pm$ tetrahedrons with one form appreciably dominant. After 36 hours there were some crystals with combinations of $\pm$ tetrahedrons equally developed. The crystals predominating were combinations of $\pm$ tetrahedrons with one form dominant. After 60 hours all the crystals were combinations of $\pm$ tetrahedrons with about 50% of the crystals having both forms equally developed while of the other 50% one form was dominant.

EVAPORATION "MEDIUM"—TEMPERATURE 20°C – 24°C

Crystals were allowed to grow under the above conditions from solutions of lead nitrate, barium nitrate and strontium nitrate. Solutions were of the following concentrations:

25 cc. H_2O

17 gm. $\text{Pb}(\text{NO}_3)_2$

20 cc. H_2O

2.2 gm. $\text{Ba}(\text{NO}_3)_2$

25 cc. H_2O

18 gm. $\text{Sr}(\text{NO}_3)_2$

Observations on each set of solutions, after crystals first appeared, were made for record after 12 hours, 36 hours, and 60

hours of crystal growth, respectively. The following results were obtained:

After 12 hours the majority of the crystals were combinations of $\pm$ tetrahedrons of equal development. An appreciable percent were $\pm$ tetrahedrons in combinations with a cube with the $\pm$ tetrahedrons equally developed and with the cube decidedly the subordinate form.

After successive intervals of 36 hours and 60 hours there was in each case an appreciable increase in the percent of crystals having $\pm$ tetrahedrons in combination with a cube. The cube was relatively larger in the case of barium nitrate than in either of the other two salts. However, it was the subordinate form.

Qualitatively the results for each salt were the same.

EVAPORATION "MEDIUM"—TEMPERATURE 25°C–30°C

Crystals were obtained from solutions of lead nitrate, barium nitrate and strontium nitrate under conditions indicated above. The solutions were of the following concentrations:

25 cc. H ₂ O	25 cc. H ₂ O	25 cc. H ₂ O
18.5 gm. Pb(NO ₃) ₂	3 gm. Ba(NO ₃) ₂	22 gm. Sr(NO ₃) ₂

LEAD NITRATE. Crystals obtained from lead nitrate solutions were observed after 12 hours, 36 hours, and 60 hours of crystal growth. In each case, from 50 to 75 crystals were grown in each solution observed for record.

After 12 hours of crystal growth the majority of crystals were combinations of the cubes and $\pm$ tetrahedrons with all three forms about equally developed. A smaller number were of the same combination, but the two tetrahedrons, equally developed, were the dominant forms. A few crystals, ten to fifteen, were of $\pm$ tetrahedrons of equal development. After 36 hours the majority of the crystals were combinations of a cube and $\pm$ tetrahedrons and a pyritohedron. The cube was the dominant form and the pyritohedron the subordinate form. The remaining crystals were combinations of a cube and $\pm$ tetrahedrons with the cube the dominant form. After 60 hours the pyritohedron was present on a larger percent of crystals than previously, and had become relatively larger but was still the subordinate form.

The results obtained with barium nitrate and strontium nitrate are indicated in table No. 1.

EVAPORATION "SLOW"—TEMPERATURE 20°C–24°C

The solutions for this experiment were of the same concentration as for those under conditions of "medium" evaporation and temperature of 20°C–24°C.

LEAD NITRATE. If lead nitrate crystals are produced under conditions of medium evaporation at temperatures of 20°C–24°C the first crystals formed are combinations of $\pm$ tetrahedrons about equally developed. If such crystals are transferred from conditions of "medium" evaporation to conditions of "slow" evaporation, there is a marked influence on the crystal habit. In less than ten minutes, cube faces begin to form on some crystals in combination with the two tetrahedrons. The first appearance is as very narrow faces bevelling the edges of the crystals. After 12 hours the cube is the dominant form on the majority of the crystals. All crystals are combinations of a cube and $\pm$ tetrahedrons. On some crystals the three forms are about equally developed, and on a small percent, the $\pm$ tetrahedrons still dominate.

During the succeeding periods of 36 hours and 60 hours the percent of crystals on which the cube is the dominant form increases. However, no other forms occur in combinations.

BARIUM NITRATE. Barium nitrate crystals grown in an aqueous solution under conditions of "slow" evaporation and temperature 20°C–24°C after 12 hours of crystal growth are qualitatively the same in habit as lead nitrate crystals grown under the same conditions. The cube is relatively larger in size and also crystals on which the cube is the dominant form occur in larger percent. After 36 hours of crystal growth, the cube becomes more completely dominant. On some crystals there is only one tetrahedron in combination. After 60 hours some crystals are single cubes, some combinations of a cube and one tetrahedron and some a cube and $\pm$ tetrahedrons with the cube decidedly dominant.

EVAPORATION "SLOW"—TEMPERATURE 25°C–30°C

Crystals from solutions of lead nitrate, barium nitrate, and strontium nitrate were allowed to grow under conditions of "slow" evaporation and temperatures of 25°C–30°C. The solutions were made of the same concentrations as for the experiments under conditions of "medium" evaporation and temperatures 25°C–30°C.

It was found an advantage in all cases to allow crystals to develop first under conditions of "medium" evaporation with temperatures of 25°C–30°C. The first crystals formed in all cases were combinations of $\pm$ tetrahedrons. As soon as crystals have formed and the desired numbers are in the liquor the dishes may be transferred to conditions of "slow" evaporation. Observations for record were made after 12 hours, 36 hours and 60 hours of crystal growth.

LEAD NITRATE. Lead nitrate crystals developed under the above conditions after 12 hours of crystal growth are combinations of a cube, $\pm$ tetrahedrons and a pyritohedron. This combination with the cube the dominant form occurs on the majority of crystals. Some crystals, however, are combinations of $\pm$ tetrahedrons and a pyritohedron. Some crystals are combinations of a cube and a pyritohedron. The pyritohedron is present on all forms. After 36 hours of crystal growth the pyritohedron becomes more prominent; it constantly grows relatively larger.

After 60 hours the pyritohedron is relatively equal in size, on some crystals, to the other forms with which it is in combination. The development of the pyritohedron under temperatures around 30°C is very pronounced.

BARIUM NITRATE. Barium nitrate crystals placed under conditions of "slow" evaporation and temperatures of 25°C–30°C react very much the same as lead nitrate crystals during the first 12 hours of crystal growth. After 36 hours the pyritohedron is relatively equal in size to the $\pm$ tetrahedrons. The cube is more generally in combination than on lead nitrate crystals and is relatively larger.

After 60 hours the crystals are all combinations of a cube, pyritohedron and $\pm$ tetrahedrons. In some experiments conducted under these conditions a few crystals grew of the combination, cube, pyritohedron, $\pm$ tetrahedrons and tetrahedral pentagonal dodecahedron. The crystals were practically perfect. The cube was the dominant form.

Table No. 1 represents in tabular form the results obtained from a set of experiments, a few of which have been described above, with crystals grown from pure aqueous solutions,

TABLE I

Salt	Rate of crystal growth	Hours of crystal growth	Temperature conditions	Results
$\text{Pb}(\text{NO}_3)_2$	"Fast"	12	20°C–24°C	All crystals $\pm$ tetrahedrons in combination.
"	"	36	"	"
"	"Medium"	12	5°C–10°C	All crystals combinations of $\pm$ tetrahedrons; one form decidedly dominant.
"	"	36	"	"
$\text{Ba}(\text{NO}_3)_2$	"	12	"	All crystals single tetrahedrons.
"	"	36	"	Predominance of single tetrahedrons; also $\pm$ tetrahedrons in combination, one form dominant.
$\text{Sr}(\text{NO}_3)_2$	"	12	"	All crystals combinations of $\pm$ tetrahedrons; one form decidedly dominant.
"	"	36	"	"
$\text{Pb}(\text{NO}_3)_2$	"	12	15°C–20°C	Predominance of $\pm$ tetrahedrons equally developed; also $\pm$ tetrahedrons, one form dominant.
"	"	36	"	Increase in predominance of $\pm$ tetrahedrons equally developed; $\pm$ tetrahedrons, one form dominant.
"	"	60	"	"
$\text{Ba}(\text{NO}_3)_2$	"	12	"	All crystals $\pm$ tetrahedrons one form dominant.
"	"	36	"	Predominance $\pm$ tetrahedrons, one form dominant. Also $\pm$ tetrahedrons equally developed.

Salt	Rate of crystal growth	Hours of crystal growth	Temperature conditions	Results
$\text{Ba}(\text{NO}_3)_2$	"Medium"	60	15°C–20°C	50% $\pm$ tetrahedrons equally developed. 50% $\pm$ tetrahedrons, one form dominant.
$\text{Sr}(\text{NO}_3)_2$	"Medium"	12	15°C–20°C	Predominance of $\pm$ tetrahedrons equally developed; also $\pm$ tetrahedrons, one form dominant.
"	"	36	"	Greater predominance of tetrahedrons equally developed. $\pm$ tetrahedrons, one form dominant.
"	"	60	"	"
$\text{Pb}(\text{NO}_3)_2$	"	12	20°C–24°C	Predominance of $\pm$ tetrahedrons equally developed; also $\pm$ tetrahedrons and cube, $\pm$ tetrahedrons dominant.
"	"	36	"	Predominance of $\pm$ tetrahedrons equally developed. Increase $\pm$ tetrahedrons and cube.
"	"	60	"	"
$\text{Ba}(\text{NO}_3)_2$	"	12	"	Predominance of $\pm$ tetrahedrons equally developed; also $\pm$ tetrahedrons and cube, tetrahedrons dominant
"	"	36	"	Same as for $\text{Pb}(\text{NO}_3)_2$; cube relatively larger.
"	"	60	"	"
$\text{Sr}(\text{NO}_3)_2$	"	12	"	Same as for $\text{Pb}(\text{NO}_3)_2$.
"	"	36	"	"
"	"	60	"	"

Salt	Rate of crystal growth	Hours of crystal growth	Temperature conditions	Results
$\text{Pb}(\text{NO}_3)_2$	"Medium"	12	25°C–30°C	Predominance of $\pm$ tetrahedrons and cube; also $\pm$ tetrahedrons and cube, $\pm$ tetrahedrons dominant; also $\pm$ tetrahedrons.
"	"	36	"	Predominance of cube, $\pm$ tetrahedrons, pyritohedron, cube dominant; also cube, $\pm$ tetrahedrons, cube dominant.
"	"	60	"	Increase in percent of pyritohedrons.
$\text{Ba}(\text{NO}_3)_2$	"	12	"	Predominance of cube, $\pm$ tetrahedrons. Also cube, $\pm$ tetrahedrons, pyritohedrons.
"	"	36	"	Increase in percent of pyritohedrons.
"	"	60	"	"
$\text{Sr}(\text{NO}_3)_2$	"	12	"	Predominance of cube, $\pm$ tetrahedrons. Also cube, $\pm$ tetrahedrons, pyritohedrons.
"	"	36	"	Increase in percent of pyritohedrons.
"	"	60	"	"
$\text{Pb}(\text{NO}_3)_2$	"Slow"	12	20°C–24°C	Predominance of cube, $\pm$ tetrahedrons, cube dominant. Cube, $\pm$ tetrahedrons, all equally developed. $\pm$ tetrahedrons and cube, tetrahedrons dominant.
"	"	36	"	Increase of cube dominance.
"	"	60	"	"

Salt	Rate of crystal growth	Hours of crystal growth	Temperature conditions	Results
Ba(NO ₃) ₂	"	12	"	Predominance of cube, ± tetrahedrons. Also cube, ± tetrahedrons, equally developed. Small percent ± tetrahedrons, cube.
"	"	36	"	Predominance of cube, ± tetrahedrons. Cube, single tetrahedron.
"	"	60	"	Predominance cube, ± tetrahedrons. Cube, single tetrahedron. Cube.
Sr(NO ₃) ₂	"	12	"	Cube, ± tetrahedrons, cube dominant.
"	"	36	"	Cube becomes more dominant.
"	"	60	"	"
Pb(NO ₃) ₂	"Slow"	12	25°C–30°C	Predominance of cube, ± tetrahedrons, pyritohedron. ± tetrahedrons, pyritohedron. Cube, pyritohedron.
"	"	36	"	Pyritohedron relatively larger.
"	"	60	"	"
Ba(NO ₃) ₂	"	12	"	Predominance of cube, ± tetrahedrons, pyritohedron. ± tetrahedrons, pyritohedron. Cube, pyritohedron.
"	"	36	"	Cube, ± tetrahedrons, pyritohedron.
"	"	60	"	Predominance of cube, pyritohedron, ± tetrahedrons. Cube, pyritohedron, ± tetrahedrons, tetrahedral pentagonal dodecahedron.

Salt	Rate of crystal growth	Hours of crystal growth	Temperature condensities	Results
$\text{Sr}(\text{NO}_3)_2$	"Slow"	12	25°C–30°C	Predominance of cube, $\pm$ tetrahedrons, pyritohedron. Cube, $\pm$ tetrahedrons.
"	"	36	"	Cube, $\pm$ tetrahedrons, pyritohedron.
"	"	60	"	Predominance of cube, $\pm$ tetrahedrons, pyritohedron. Cube, pyritohedron, $\pm$ tetrahedrons.

SUMMARY AND CONCLUSIONS OF CRYSTALLIZATION FROM PURE AQUEOUS SOLUTIONS

The results obtained from the experiments reported above point very strongly to the conclusion that the crystal habit of crystals from pure aqueous solutions may be influenced in a marked manner by:

1. The rate of crystal growth;
2. The temperature of crystal growth,

Crystals growing at a rapid rate have a tendency to develop as simple forms, even at high temperatures. Crystals formed at any temperature below the boiling point of the aqueous solutions of the salts used, under ordinary pressure conditions, if grown rapidly, are developed as simple forms. In the case of the salts lead nitrate, barium nitrate and strontium nitrate, the crystals formed rapidly at high temperatures are combinations of $\pm$ tetrahedrons equally developed so that the crystals resemble small octahedrons.

If the rate of crystal growth is slow the temperature at which crystals develop seems to be a very strong factor in determining crystal habit. This is very evident from all the results obtained and especially so in the case of barium nitrate. Single tetrahedrons were developed at temperatures of 5°C–10°C and at temperatures between 25°C and 30°C complex crystals of a cube, pyritohedron, $\pm$ tetrahedrons and a tetrahedral pentagonal dodecahedron were obtained.

Observations of the influence of temperature on crystal habit have been recorded in scientific literature; however, reports of systematic work on this subject have not been found.

Levy and Lacroix⁷ in describing Boricky's method of procedure in micro-chemical analysis report that the temperature at which crystallization is allowed to proceed has a perceptible influence on the crystal form of the hydrofluosilicate obtained. George Kalb⁸ states that among ice crystals formed near 0°C the tabular habit prevails, while lower temperatures favor the production of the prismatic habit.

If crystals of a complex habit formed at a temperature near 30°C and slow rate of crystal growth are suddenly changed to conditions of rapid crystal growth, while still in the mother liquor, either by suddenly lowering the temperature or by means of rapid evaporation, they are rapidly changed to crystals of simple habit. The complex forms may often be seen enclosed in the nature of a phantom crystal in the simple crystals of $\pm$ tetrahedrons.

It has been suggested that the change in viscosity of an aqueous solution due to a change in temperature is a factor that should be considered as influencing crystal habit. This is undoubtedly a very valuable suggestion. Since the interpretations offered do not, at present, seem to fit the results obtained, and as a careful consideration of this factor is a problem in itself it has been left open for future consideration.

A very interesting observation has been reported by Hostetter,⁹ that if the solvent action on octahedrons of alum crystals caused a rounding of edges, the rhombic dodecahedron was formed in combination with the octahedron when crystal growth was resumed. The action of solution of a similar nature has been observed in this work. The form which resulted, however, after crystal growth was resumed was determined by the temperature of the solution.

Tutton's idea of "over crystallization"¹⁰ seems to be well substantiated in practically all of the results obtained from conditions of "medium" rate of crystal growth. In fact results obtained from all other conditions of evaporation, "medium" or "slow" and at temperatures between 20° to 30°C may be considered to substantiate it.

⁷ Levy and Lacroix: *Les Mineraux des Roches*, p. 125.

⁸ *Centr. Min. Geol.*, 1921, pp. 129-34.

⁹ J. C. Hostetter: *Jour. Wash. Acad. of Science*, Vol. 9, Nov. 4, pp. 93.

¹⁰ A. E. H. Tutton: *Crystallography and Practical Crystal Measurement*, Vol. 1, pp. 16-17.

In all cases the crystals at first are of a simpler habit than after a period of 36 hours and 60 hours of crystal growth. According to Tutton, when crystals are first formed the process of crystallization proceeds so rapidly that it continues until the concentration of the solution has become lower than the theoretical state of equilibrium. Since crystallization in these experiments resulted because of evaporation the state of equilibrium was undoubtedly restored before solvent action took place sufficiently to cause a rounding of the edges as Tutton observes.

Tutton's idea explains very nicely why the crystal habit should become more complex after the first few hours of crystal growth, provided the temperature is above the point where simple crystals form. If the state of concentration has been reduced below the theoretical state of equilibrium, it seems quite likely that as the solution approaches a state of supersaturation, brought on by evaporation, the presence of a number of crystals of appreciable size will make it quite impossible for the solution to again reach a very high state of supersaturation. The process of crystallization will continue the moment the state of saturation exceeds the theoretical state of equilibrium. Under conditions of "medium" or "slow" evaporation the rate of crystal growth will, therefore, undoubtedly progress much more slowly after the first few hours of crystal growth or after the state of "over crystallization" has been obtained, than before that time. If the temperature, then, is high enough the crystals will, because of a slower rate of crystal growth, be more complex in habit.

The word "complex" is used quite frequently in this paper and in conformity with general usage is employed to distinguish simple crystals of one form from crystals of two or more forms. A crystal of the $\pm$ tetrahedrons in combination with a cube, for instance, is referred to as being more complex than a crystal of just $\pm$ tetrahedrons. However, a crystal of a more complex parametral ratio is regarded as more complex than a crystal expressed by a simple parametral ratio. The pyritohedron (hko) is regarded as more complex, therefore, than either the tetrahedron (111) or the cube (100). Likewise, a combination of a cube and a pyritohedron would be regarded as a more complex crystal than a cube in combination with either one or two tetrahedrons.

The results obtained in these experiments indicate that the pyritohedron is formed to advantage at a higher temperature

than the cube or the tetrahedrons. The cube, likewise, forms at a slightly higher temperature than the $\pm$ tetrahedrons, and the combination of the $\pm$ tetrahedrons forms at a higher temperature than the single tetrahedron. The rate of evaporation for each case is considered "slow."

A combination of crystal forms, in the light of the above experiments, may for some crystals be considered to be the result of a successive change of conditions. If conditions favorable to any one crystal form exist for a sufficiently long period of time that form will be the dominant form or it may even grow as a single form to the exclusion of all other forms. This result has been obtained in the case of the cube. The most favorable temperature for the cube of barium nitrate seems to be about 23°C. If this temperature can be successfully maintained for a period of three days, the majority of the barium nitrate crystals in the mother liquor will be cubes. Such results have been obtained repeatedly.

B. CRYSTALS FORMED IN AQUEOUS SOLUTIONS CONTAINING ONE FOREIGN SUBSTANCE

To determine the effect of foreign substances, or impurities, on crystal habit a series of experiments was carried out testing the influence of a number of inorganic salts which differ somewhat in solubility. Also, some organic substances were used as impurities. Some insoluble substances reduced to a very fine powder were likewise used as suspensions. The experiments in which inorganic salts were used as impurities will be described first.

Experiments were conducted with the same three salts listed under A, viz: lead nitrate, barium nitrate, and strontium nitrate. Four different conditions for crystal growth were employed:

1. Evaporation "medium"; temperature 20°C to 24°C.
2. Evaporation "medium"; temperature 25°C to 30°C.
3. Evaporation "slow"; temperature 20°C to 24°C.
4. Evaporation "slow"; temperature 25°C to 30°C.

Observations for record were made after 12 hours, 36 hours, and 60 hours of crystal growth. Experiments were conducted in the same manner as under A. The results obtained from a few experiments will be briefly described in the following pages. Other results from a number of these experiments using inorganic salts as impurities will be tabulated in table No. III.

It was found that within certain limits, the result obtained was influenced by the amount of impurity added. In order, therefore,

to make comparisons more valuable, equivalent amounts of the impurities were used.

Barium nitrate was added as an impurity to a solution of lead nitrate. Because of its low solubility the amount employed was not equivalent to that of the other salts used. The amount of barium nitrate added was the amount necessary to make a $1/7$ normal solution. For all other salts, unless otherwise indicated, an amount sufficient for a $2/5$ normal solution was used. For the sake of making comparisons it was found that results were more consistent and more pronounced by using that amount or more. Appreciable results were obtained by adding the amounts required for a $1/10$ normal solution.

LEAD NITRATE + SILVER NITRATE
Evaporation "medium"
Temperature 25°C to 30°C

All the crystals that were first formed under these conditions were combinations of $\pm$ tetrahedrons, about equally developed. After 12 hours of crystal growth some of the crystals began to show a small pyritohedron in combination with the $\pm$ tetrahedrons and as crystal growth was allowed to continue the pyritohedrons steadily increased in number and also became relatively larger. The tetrahedrons, however, remained the dominant forms.

If this experiment is performed at temperatures of 20°C to 24°C it will be found that for the first 12 hours the same results are obtained as with temperatures of 25°C to 30°C . As crystal growth is allowed to continue under temperature conditions of 20°C to 30°C the form to appear first in combination with the $\pm$ tetrahedrons is the cube. If the process of crystal growth continues for 10 or 15 hours, after the cube has entered into combination with the majority of the crystals, the pyritohedron may develop on a small percent of crystals as a very subordinate form.

LEAD NITRATE + SILVER NITRATE
Evaporation "slow"
Temperature 25°C to 30°C .

Crystals first started under conditions of "medium" evaporation are transferred to conditions of "slow" evaporation. The crystals first formed are combinations of $\pm$ tetrahedrons. In a few hours after changing from "medium" conditions to "slow" conditions of

evaporation, the crystals become more complex and after 36 hours of crystal growth the pyritohedron is relatively larger than for the same period of time under conditions of "medium" evaporation. The cube is present as a subordinate form on a small percent of crystals. After 60 hours of crystal growth the pyritohedron has increased in relative size.

By comparing these results with those obtained when lead nitrate crystals are grown in pure aqueous solutions a pronounced contrast may readily be noted. For the same conditions of evaporation and temperature there is a decided tendency for the crystals, of the experiment just described, to be more simple in habit than crystals from pure aqueous solutions. The tendency for crystals of simple habit to form is stronger during the first 12 hours of crystal growth than for a longer period of growth. After 60 hours, the crystals from aqueous solutions, with silver nitrate as an impurity, become as complex as those from pure aqueous solutions. The complex forms from pure aqueous solutions, however, occur in relatively higher percent.

The presence of silver nitrate in solutions of barium nitrate or strontium nitrate has qualitatively the same effect on the habit of the crystals obtained as in the case of lead nitrate.

If crystal growth is allowed to continue for 60 hours or more, the crystals in the liquor gradually become more complex in habit. The crystals finally obtained under conditions of "slow" evaporation and at temperatures between 25°C and 30°C are as complex as those obtained from pure aqueous solutions under the same conditions and for the same period of crystal growth.

TABLE NO. III

LEAD NITRATE; EVAPORATION "MEDIUM"; TEMPERATURE 20°C to 24°C.

Impurity	Hours of Crystal Growth	Percent predominance	Percent dominance
AgNO ₃	12	± (111).....100%	Equally developed
AgNO ₃	36	± (111)..... 75% ± (111), (100)..... 25%	± (111).....100%
AgNO ₃	60	± (111)..... 60% ± (111), (100)..... 40%	± (111)..... 75% (100)..... 25%
NH ₄ NO ₃	12	± (111).....100%	Equally developed
NH ₄ NO ₃	36	± (111)..... 63% ± (111), (100)..... 37%	± (111).....100%
NH ₄ NO ₃	60	± (111)..... 60% ± (111), (100)..... 40%	± (111)..... 80% (100)..... 20%
Ca(NO ₃) ₂	12	± (111).....100%	Equally developed
Ca(NO ₃) ₂	36	± (111)..... 60% ± (111), (100)..... 40%	± (111).....100%
Ca(NO ₃) ₂	60	± (111)..... 55% ± (111), (100)..... 45%	± (111)..... 67% (100)..... 33%
Cu(NO ₃) ₂	12	± (111)..... 95% ± (111), (100)..... 5%	± (111).....100%
Cu(NO ₃) ₂	36	± (111)..... 50% ± (111), (100)..... 50%	± (111).....100%
Cu(NO ₃) ₂	60	± (111)..... 48% ± (111), (100)..... 52%	± (111)..... 60% (100)..... 40%

LEAD NITRATE; EVAPORATION "MEDIUM"; TEMPERATURE 20°C TO 24°C.

Impurity	Hours of Crystal Growth	Percent predominance	Percent dominance
NaNO ₃	12	±(111) 100%	Equally developed
NaNO ₃	36	±(111) 75% ±(111), (100) 25%	±(111) 100%
NaNO ₃	60	±(111) 68% ±(111), (100) 32%	±(111) 90% (100) 10%
Mg(NO ₃) ₂	12	±(111) 85% ±(111), (100) 15%	±(111) 100%
Mg(NO ₃) ₂	36	±(111) 80% ±(111), (100) 20%	±(111) 93% (100) 7%
Mg(NO ₃) ₂	60	±(111) 75% ±(111), (100) 25%	±(111) 88% (100) 12%
LiNO ₃	12	±(111) 100%	Equally developed
LiNO ₃	36	±(111) 82% ±(111), (100) 18%	±(111) 100%
LiNO ₃	60	±(111) 30% ±(111), (100) 70%	±(111) 80% (100) 20%
KNO ₃	12	±(111) 80% ±(111), (100) 20%	±(111) 100%
KNO ₃	36	±(111) 65% ±(111), (100) 35%	±(111) 100%
KNO ₃	60	±(111) 35% ±(111), (100) 65%	±(111) 78% (100) 22%
Ba(NO ₃) ₂	12	±(111) 30% ±(111), (100) 70%	±(111) 85% (100) 15%
Ba(NO ₃) ₂	36	±(111) 28% ±(111), (100) 72%	±(111) 83% (100) 17%
Ba(NO ₃) ₂	60	±(111) 20% ±(111), (100) 80%	±(111) 80% (100) 20%

LEAD NITRATE; EVAPORATION "SLOW"; TEMPERATURE 25°C TO 30°C.

Impurity	Hours of Crystal Growth	Percent predominance	Percent dominance
AgNO ₃	12	± (111)..... 80% ± (111), (100)..... 8% ± (111), (hko)..... 12%	± (111).....100%
AgNO ₃	36	± (111)..... 30% ± (111), (100)..... 30% ± (111), (hko)..... 40%	± (111).....100%
AgNO ₃	60	± (111)..... 18% ± (111), (100), (hko) . 50% ± (111), (hko)..... 32%	± (111)..... 80% (100)..... 12% ± (111), (hko)..... 8%
NH ₄ NO ₃	12	± (111)..... 83% ± (111), (100)..... 12% ± (111), (100), (hko) . 5%	± (111).....100%
NH ₄ NO ₃	36	± (111)..... 13% ± (111), (100)..... 28% ± (111), (100), (hko) . 59%	± (111)..... 90% (100)..... 3% ± (111), (hko)..... 7%
NH ₄ NO ₃	60	± (111)..... 3% ± (111), (100)..... 35% ± (111), (hko)..... 12% ± (111), (100), (hko) . 50%	± (111)..... 85% (100)..... 8% ± (111), (hko)..... 7%
Ca(NO ₃) ₂	12	± (111)..... 70% ± (111), (100)..... 12% ± (111), (100), (hko) . 18%	± (111).....100%
Ca(NO ₃) ₂	36	± (111)..... 7% ± (111), (100)..... 35% ± (111), (hko)..... 15% ± (111), (100), (hko) . 43%	± (111)..... 87% (100)..... 5% ± (111), (hko)..... 8%
Ca(NO ₃) ₂	60	± (111)..... 5% ± (111), (100)..... 35% ± (111), (hko)..... 20% ± (111), (100), (hko) . 40%	± (111)..... 75% (100)..... 10% ± (111), (hko)..... 15%

LEAD NITRATE; EVAPORATION "SLOW"; TEMPERATURE 25°C TO 30°C.

Impurity	Hours of Crystal Growth	Percent predominance	Percent dominance
$\text{Cu}(\text{NO}_3)_2$	12	$\pm(111)$ 63%	$\pm(111)$ 100%
		$\pm(111), (100)$ 18%	
		$\pm(111), (\text{hko})$ 7%	
		$\pm(111), (100), (\text{hko})$. 12%	
$\text{Cu}(\text{NO}_3)_2$	36	$\pm(111)$ 10%	$\pm(111)$ 80%
		$\pm(111), (100)$ 27%	(100)..... 8%
		$\pm(111), (\text{hko})$ 13%	$\pm(111), (\text{hko})$ 12%
		$\pm(111), (100), (\text{hko})$. 50%	
$\text{Cu}(\text{NO}_3)_2$	60	$\pm(111)$ 0%	$\pm(111)$ 68%
		$\pm(111), (100)$ 43%	(100)..... 18%
		$\pm(111), (\text{hko})$ 15%	$\pm(111), (\text{hko})$ 14%
		$\pm(111), (100), (\text{hko})$. 42%	
NaNO_3	12	$\pm(111)$ 55%	$\pm(111)$ 100%
		$\pm(111), (100)$ 30%	
		$\pm(111), (\text{hko})$ 7%	
		$\pm(111), (100), (\text{hko})$. 8%	
NaNO_3	36	$\pm(111)$ 8%	$\pm(111)$ 77%
		$\pm(111), (100)$ 32%	(100)..... 5%
		$\pm(111), (\text{hko})$ 8%	$\pm(111), (\text{hko})$ 18%
		$\pm(111), (100), (\text{hko})$. 52%	
NaNO_3	60	$\pm(111)$ 5%	$\pm(111)$ 65%
		$\pm(111), (100)$ 50%	$\pm(111), (\text{hko})$ 35%
		$\pm(111), (\text{hko})$ 20%	
		$\pm(111), (100), (\text{hko})$. 25%	
$\text{Mg}(\text{NO}_3)_2$	12	$\pm(111)$ 28%	$\pm(111)$ 78%
		$\pm(111), (100)$ 30%	$\pm(111), (\text{hko})$ 20%
		$\pm(111), (\text{hko})$ 22%	$\pm(111), (100), (\text{hko})$. 2%
		$\pm(111), (100), (\text{hko})$. 20%	
$\text{Mg}(\text{NO}_3)_2$	36	$\pm(111)$ 12%	$\pm(111)$ 48%
		$\pm(111), (100)$ 32%	$\pm(111), (100)$ 10%
		$\pm(111), (\text{hko})$ 16%	$\pm(111), (100), (\text{hko})$. 12%
		$\pm(111), (100), (\text{hko})$. 40%	$\pm(111), (\text{hko})$ 30%
$\text{Mg}(\text{NO}_3)_2$	60	$\pm(111)$ 8%	$\pm(111)$ 57%
		$\pm(111), (100)$ 30%	$\pm(111), (100)$ 7%
		$\pm(111), (\text{hko})$ 32%	$\pm(111), (\text{hko})$ 30%
		$\pm(111), (100), (\text{hko})$. 30%	$\pm(111), (100), (\text{hko})$. 6%

LEAD NITRATE; EVAPORATION "SLOW"; TEMPERATURE 25°C TO 30°C.

Impurity	Hours of Crystal Growth	Percent predominance	Percent dominance
LiNO ₃	12	$\pm(111)$ 32% $\pm(111), (100)$ 30% $\pm(111), (hko)$ 25% $\pm(111), (100), (hko)$. 23%	$\pm(111)$ 85% $\pm(111), (hko)$ 8% $\pm(111), (100), (hko)$ 7%
LiNO ₃	36	$\pm(111)$ 15% $\pm(111), (100)$ 28% $\pm(111), (hko)$ 17% $\pm(111), (100), (hko)$. 40%	$\pm(111)$ 50% $\pm(111), (100)$ 15% $\pm(111), (hko)$ 35% $\pm(111), (100), (hko)$ 10%
LiNO ₃	60	$\pm(111)$ 10% $\pm(111), (100)$ 35% $\pm(111), (hko)$ 32% $\pm(111), (100), (hko)$. 23%	$\pm(111)$ 60% $\pm(111), (100)$ 10% $\pm(111), (hko)$ 25% $\pm(111), (100), (hko)$ 5%
KNO ₃	12	$\pm(111)$ 23% $\pm(111), (100)$ 35% $\pm(111), (hko)$ 22% $\pm(111), (100), (hko)$. 20%	$\pm(111)$ 70% $\pm(111), (100)$ 5% $\pm(111), (hko)$ 15% $\pm(111), (100), (hko)$ 10%
KNO ₃	36	$\pm(111)$ 13% $\pm(111), (100)$ 32% $\pm(111), (hko)$ 20% $\pm(111), (100), (hko)$. 35%	$\pm(111)$ 47% $\pm(111), (100)$ 20% $\pm(111), (hko)$ 30% $\pm(111), (100), (hko)$ 3%
KNO ₃	60	$\pm(111)$ 5% $\pm(111), (100)$ 30% $\pm(111), (hko)$ 28% $\pm(111), (100), (hko)$. 37%	$\pm(111)$ 35% $\pm(111), (100)$ 15% $\pm(111), (hko)$ 38% $\pm(111), (100), (hko)$ 12%
Ba(NO ₃) ₂	12	$\pm(111), (100)$ 42% $\pm(111), (hko)$ 30% $\pm(111), (100), (hko)$. 28%	$\pm(111)$ 40% $\pm(111), (100)$ 15% $\pm(111), (hko)$ 40% $\pm(111), (100), (hko)$ 5%
Ba(NO ₃) ₂	36	$\pm(111), (100)$ 35% $\pm(111), (hko)$ 23% $\pm(111), (100), (hko)$. 42%	$\pm(111)$ 30% $\pm(111), (100)$ 25% $\pm(111), (hko)$ 45%
Ba(NO ₃) ₂	60	$\pm(111), (100)$ 25% $\pm(111), (hko)$ 20% $\pm(111), (100), (hko)$. 55%	$\pm(111)$ 22% $\pm(111), (100)$ 33% $\pm(111), (hko)$ 40% $\pm(111), (100), (hko)$ 5%

BARIUM NITRATE; EVAPORATION "SLOW"; TEMPERATURE 25°C TO 30°C.

Impurity	Hours of Crystal Growth	Percent predominance	Percent dominance
AgNO ₃	12	± (111) 88% ± (111), (100) 12%	± (111) 100%
AgNO ₃	36	± (111) 50% ± (111), (100) 43% ± (111), (100), (hko) . 7%	± (111) 45% ± (111), (100) 20% ± (111), (hko) 35%
AgNO ₃	60	± (111) 20% ± (111), (100) 45% ± (111), (100), (hko) . 35%	± (111) 40% (100) 5% ± (111), (100) 12% ± (111), (hko) 43%
NH ₄ NO ₃	12	± (111) 90% ± (111), (100) 10%	± (111) 100%
NH ₄ NO ₃	36	± (111) 48% ± (111), (100) 50% ± (111), (100), (hko) . 2%	± (111) 50% ± (111), (100) 25% ± (111), (hko) 25%
NH ₄ NO ₃	60	± (111) 25% ± (111), (100) 43% ± (111), (100), (hko) . 32%	± (111) 47% ± (111), (100) 20% ± (111), (hko) 33%
Ca(NO ₃) ₂	12	± (111) 80% ± (111), (100) 20%	± (111) 80% ± (111), (100) 20%
Ca(NO ₃) ₂	36	± (111) 45% ± (111), (100) 53% ± (111), (100), (hko) . 2%	± (111) 43% ± (111), (100) 20% ± (111), (hko) 37%
Ca(NO ₃) ₂	60	± (111) 17% ± (111), (100) 40% ± (111), (100), (hko) . 43%	± (111) 50% ± (111), (100) 25% ± (111), (hko) 25%
Cu(NO ₃) ₂	12	± (111) 73% ± (111), (100) 24% ± (111), (100), (hko) . 3%	± (111) 100%
Cu(NO ₃) ₂	36	± (111) 45% ± (111), (100) 47% ± (111), (100), (hko) . 8%	± (111) 35% ± (111), (100) 30% ± (111), (hko) 35%

BARIUM NITRATE; EVAPORATION "SLOW"; TEMPERATURE 25°C TO 30°C.

Impurity	Hours of Crystal Growth	Percent predominance	Percent dominance
Cu(NO ₃) ₂	60	± (111)..... 12%	± (111)..... 25%
		± (111), (100)..... 48%	± (111), (100)..... 37%
		± (111), (100), (hko). 40%	± (111), (hko)..... 38%
NaNO ₃	12	± (111)..... 70%	± (111)..... 100%
		± (111), (100)..... 25%	
		± (111), (100), (hko). 5%	
NaNO ₃	36	± (111)..... 35%	± (111)..... 35%
		± (111), (100)..... 47%	± (111), (100)..... 30%
		± (111), (100), (hko). 18%	± (111), (hko)..... 35%
NaNO ₃	60	± (111)..... 0%	± (111)..... 7%
		± (111), (100)..... 40%	± (111), (100)..... 38%
		± (111), (100), (hko). 60%	± (111), (hko)..... 55%
Mg(NO ₃) ₂	12	± (111)..... 52%	± (111)..... 92%
		± (111), (100)..... 35%	± (111), (100)..... 8%
		± (111), (100), (hko). 13%	
Mg(NO ₃) ₂	36	± (111)..... 22%	± (111)..... 20%
		± (111), (100)..... 55%	± (111), (100)..... 47%
		± (111), (100), (hko). 23%	± (111), (hko)..... 33%
Mg(NO ₃) ₂	60	± (111), (100)..... 53%	± (111)..... 3%
		± (111), (100), (hko). 47%	± (111), (100)..... 45%
			± (111), (hko)..... 55%
LiNO ₃	12	± (111)..... 60%	± (111)..... 100%
		± (111), (100)..... 32%	
		± (111), (100), (hko). 8%	
LiNO ₃	36	± (111)..... 28%	± (111)..... 25%
		± (111), (100)..... 60%	± (111), (100)..... 50%
		± (111), (100), (hko). 12%	± (111), (hko)..... 25%
LiNO ₃	60	± (111), (100)..... 48%	± (111)..... 8%
		± (111), (100), (hko). 52%	± (111), (100)..... 50%
			± (111), (hko)..... 42%

BARIUM NITRATE; EVAPORATION "SLOW"; TEMPERATURE 25°C TO 30°C.

Impurity	Hours of Crystal Growth	Percent predominance	Percent dominance
KNO ₃	12	± (111)..... 40%	± (111)..... 82%
		± (111), (100)..... 47%	± (111), (100)..... 18%
		± (111), (100), (hko). 13%	
KNO ₃	36	± (111)..... 17%	± (111)..... 30%
		± (111), (100)..... 53%	± (111), (100)..... 37%
		± (111), (100), (hko). 30%	± (111), (hko)..... 37%
KNO ₃	60	± (111), (100)..... 37%	± (111)..... 2%
		± (111), (100), (hko). 63%	± (111), (100)..... 33%
			± (111), (hko)..... 65%

EXPLANATION OF TABLE NO. III

An explanation of Table No. III can well be made by referring to a specific result indicated in the table. On page 262, the third horizontal column of data from the top indicates the results obtained by growing lead nitrate crystals from an aqueous solution to which some silver nitrate had been added as an impurity. Crystals were grown under conditions of "medium" rate of evaporation and at temperatures ranging from 20°C to 24°C. Observations were made after the crystals had been growing for 60 hours. The result was that 60% of the crystals were ± tetrahedrons in combination, and 40% of the crystals were ± tetrahedrons in combination with a cube. Of 75% of all the crystals the ± tetrahedrons were regarded as dominant and of 25% of all the crystals the cube was dominant. In determining the percent of dominance of ± tetrahedrons, it was considered that of crystals which were combinations of just the two tetrahedrons the tetrahedrons were dominant. These were counted in with the crystals which were combinations of ± tetrahedrons and a cube of which the tetrahedrons were dominant. The ± tetrahedrons are always considered to be equally developed. When they are not equally developed it will be indicated.

The table suggests rather strongly that the influence of the inorganic salts was determined to some extent by their relative solubility. When a salt present as an impurity is more soluble than the salt forming into crystals, the effect is to increase the tendency

to form crystals of simple habit. If the salt present as an impurity is less soluble than the one whose crystals are growing the effect is to cause a tendency to form crystals of a more complex habit. Sodium nitrate, lithium nitrate, and potassium nitrate indicate a stronger influence to produce crystals of simple habit than would be expected by comparing their respective solubilities with some of the other salts such as copper nitrate, zinc nitrate and nickel nitrate. This suggests that there is undoubtedly another property besides solubility which should be considered.

ORGANIC COMPOUNDS

In addition to the list of experiments showing the effect of inorganic salts on the habit of crystals of lead nitrate, barium nitrate, and strontium nitrate, a series of experiments was carried out in which the following organic compounds were used as impurities:

Methylene blue
Urea
Picric acid

METHYLENE BLUE

LEAD NITRATE+METHYLENE BLUE. Methylene blue was added to solutions of lead nitrate and crystals of lead nitrate were allowed to grow under the following conditions:

Evaporation "medium"
Temperature 15° to 20°C.
Temperature 20° to 24°C.
Temperature 25° to 30°C.
Evaporation "slow"
Temperature 15° to 20°C.
Temperature 20° to 25°C.
Temperature 25° to 30°C.

Observations of results of each of the above experiments were made for record at the end of each of the following periods of time after crystals were first observed: 12 hours, 36 hours, 60 hours.

No. 1.—Evaporation "medium"; Temperature 15° to 20°C.

All lead nitrate crystals are cubes that are formed from a solution in which a small amount of methylene blue is present as an impurity if conditions are of "medium" evaporation, and temperatures between 15° and 20° C. The crystals appear as cubes from the time they can first be seen with a 20 power binocular micro-

scope. They continue to grow as cubes for periods of 36 and 60 hours.

No. 2.—Evaporation “medium”; Temperature 20° to 24°C.

The lead nitrate crystals formed under conditions of No. 2 begin as cubes and continue as such for a period of 12 hours. After 36 hours of crystal growth some of the crystals of the original crop are combinations of a cube and $\pm$ tetrahedrons. The cube in all cases is the dominant form. After 60 hours the pyritohedron is in combination as a decidedly subordinate form on some crystals.

No. 3.—Evaporation “medium”; Temperature 25° to 30°C.

Crystals of lead nitrate formed under conditions represented under No. 3 after the first 12 hours are a mixture of cubes and cubes in combination with $\pm$ tetrahedrons. The cube is the dominant form. Crystals of single cubes predominate in number. After 48 hours some crystals are combinations of a cube, $\pm$ tetrahedrons and a pyritohedron. The cube is still the dominant form. The pyritohedron has increased relatively in number after 60 hours of crystal growth, and is as abundant in the combination as the $\pm$ tetrahedrons.

If the above experiments are repeated by allowing “slow” evaporation in each case instead of “medium” there is no difference to be noticed in No. 1. In No. 2 there is an increase in the percent of crystals having $\pm$ tetrahedrons in combination and in No. 3 there is an increase in the percent of crystals having the pyritohedron in combination. The pyritohedron form is also relatively larger. In over 50% of the crystals it is relatively larger than the tetrahedrons.

BARIUM NITRATE + METHYLENE BLUE. STRONTIUM NITRATE + METHYLENE BLUE. The results obtained with barium nitrate and methylene blue and with strontium nitrate and methylene blue are qualitatively the same as with lead nitrate under the same conditions. In each case satisfactory results are more difficult to obtain than with lead nitrate.

Gaubert¹¹ has reported results with lead nitrate and methylene blue and also with strontium nitrate and methylene blue. He reports that the influence of methylene blue on crystals of these salts is to produce cubes. The results reported by him may be obtained under conditions of “fast” or “medium” rates of evaporation and temperatures of 15° to 22°C and for a period of 10 or 12 hours

¹¹Paul Gaubert: *Revue Scientifique*, Paris, No. 3. Jan. 15, 1910.

of crystal growth. These results are obtained with a very small amount of methylene blue in solution.

Modifications in crystal habit are produced more easily with weak solutions of methylene blue than with concentrated solutions. Crystals in general are colored blue due to inclusions of the dye. The depth of color depends somewhat upon the concentration of methylene blue, and also somewhat on the rate of crystal growth. Crystals grown in a rapidly cooling solution are quite generally colorless and transparent.

Gaubert considers the cube habit to be due to the fact that the included methylene blue is arranged parallel to the cube faces. Crystals have been obtained, however, in the form of cubes that were colorless and transparent. Many crystals have also been obtained with small patches of blue scattered irregularly throughout the crystals. There seemed to be no orderly manner of arrangement. Microscopic examinations of crushed crystals show that some of the included methylene blue is faintly doubly refracting. The largest amount appears to be amorphous and with no special order of arrangement.

STRIATIONS. Crystals of lead nitrate and of barium nitrate grown from aqueous solutions containing methylene blue may show striations on the cube faces. These striations are of interest because they may occur arranged parallel to the cube edges, as in the case of pyrite, or they may occur diagonally arranged on the cube faces as in the case of sphalerite. When arranged in a diagonal manner they are parallel to the edges between faces of a tetrahedron and the cube. The striations parallel to the cube edges are, obviously, parallel to the edges between the faces of a pyritohedron and the cube.

It is of interest to note that crystals do not always show striations. When they are to be found on any of the crystals resulting from an experiment they usually occur on the majority or all of the crystals of that same experiment. Several experiments have been conducted to determine the cause of these striations and also a reason for their being arranged parallel to the edges between the cube and a pyritohedron for one set of crystals and in a diagonal manner for another set of crystals. The results obtained suggest very strongly that striations parallel to the edges between the cube and a pyritohedron are formed under conditions which would be more favorable to the pyritohedron than the cube in a pure aqueous

solution. The conditions, however, are not the most favorable that are possible for the development of the pyritohedron. Three or four degrees higher temperature would be more favorable. Because of a condition in the solution produced by the presence of methylene blue the cube develops instead of the pyritohedron. There is, however, a constant tendency for the pyritohedron to form. The striations indicate the places where it existed in each case for a comparatively short time.

When crystals are allowed to develop at temperatures three or four degrees higher, in other words, at 28° to 30°C instead of 24° to 26°C, the cube faces will not be found to show striations. If crystals are allowed to grow for two or three weeks at temperatures of 28° to 30°C under conditions of "slow" evaporation, the pyritohedron will become decidedly dominant. After the first few hours of crystal growth the pyritohedron continues to grow without being interrupted.

The diagonal striations form to the best advantage at temperatures below 21°C. These temperatures are more favorable to the development of the tetrahedron than the cube in a pure aqueous solution. The conditions imposed on the solution by the presence of methylene blue, however, cause the cube constantly to interrupt the growth of the tetrahedron. The striations mark the places at which the tetrahedron had a temporary existence.

A close examination of these striations reveals the fact that they are not at all uniform in dimension. In many cases a sufficient amount of the pyritohedron faces or tetrahedron faces is present to be readily recognized.

These results corroborate the idea advanced by Wherry¹² that surface phenomena do not always indicate the symmetry or internal structure of crystals. If the symmetry of lead nitrate and of barium nitrate, as suggested by their crystal forms, is correct, there are no planes of symmetry. The striations formed on the surface of the cube faces would indicate that some crystals possess axial planes of symmetry and other crystals diagonal planes of symmetry. From this it seems that it is not safe to infer the symmetry of a crystalline substance from one type of striations. Having obtained both types, as in this case, even though they do not occur on the same set of crystals, it is evident that the true symmetry is indicated.

¹²Edgar T. Wherry: *Am. Mineral.*, 9, pp. 53-54.

The above results suggest further that the striations found on crystals occurring in nature such as are characteristic of pyrite and topaz, may be there because the temperature condition favorable to one crystal form was counteracted by the presence of impurities. Due to the presence of impurities a form developed which would not have developed ordinarily under the prevailing temperature condition. There resulted a constant struggle for existence between two forms and the striations indicate the places where one form was temporarily in existence.

UREA

The effect of urea on the crystal habit of lead nitrate, barium nitrate and strontium nitrate is to produce simple forms. During the first 36 hours after crystals have formed at temperatures of 20° to 24°C and at a "slow" rate of evaporation, the forms are more predominantly the $\pm$ tetrahedrons than would be the case in a pure aqueous solution. At the higher temperatures of 25° to 30°C and especially after 60 hours of crystal growth the crystals are of a highly complex character, with combinations of the cube, pyritohedron and $\pm$ tetrahedrons.

VISCOSITY

LEAD NITRATE + GLYCERINE. In order to determine the effect of the viscosity or of thickening of the liquid on the habit of the crystals of lead nitrate, barium nitrate and strontium nitrate, 15cc. of glycerine were added to a 25cc. solution of a salt. In each case, under conditions of "medium" evaporation and at temperatures of 20° to 25°C, at the end of 48 hours all of the crystals were combinations of a cube, $\pm$ tetrahedrons and a pyritohedron.

With lead nitrate under conditions of "medium" evaporation and temperatures above 25°C, a striking result was obtained that was not obtained with any other set of experiments. The plus and minus forms of the pyritohedron developed in combination with a cube and two tetrahedrons upon a number of crystals. These results indicate very strongly that in a liquid of high viscosity there is a strong tendency for crystals to be represented by the most complex forms possible on the substance so crystallizing, if temperature conditions are proper.

¹³J. W. Retgers: Über den Einfluss fremder Substanzen in der Lösung auf die Form, die Reinheit und die Grösse der ausgeschieden Krystalle. *Zeit. Phy. Chem.*, 9, 267, (1892).

J. W. Retgers¹³ reports that by thickening the solution through the addition of gelatine, dextrine, or glycerine, there is a tendency for the promotion of skeletal growth and satisfactory results are not obtained. The results with dextrine or sugar obtained in this work confirm Retgers' results; however, those obtained with glycerine were very satisfactory.

Allowing the solution to cool suddenly from a temperature above 25°C to a temperature below 20°C had the result of changing the habit of all the crystals (75 in number) from the complex habit to a simple habit of $\pm$ tetrahedrons. The complex forms were enclosed as phantom crystals.

BARIUM NITRATE IN AGAR-AGAR. Barium nitrate crystals were produced in agar-agar by mixing a solution of barium chloride with agar-agar and then, after the agar-agar had set as a thick gel, a solution of sodium nitrate was poured over the top. The two solutions mixed by slow diffusion. The experiment was conducted under temperature conditions above 25°C. Crystals were grouped throughout the gel in arborescent fashion and the crystals in general were considerably distorted. The forms in combination on practically all of the crystals after crystal growth had been going on for a period of five weeks were $\pm$ tetrahedrons as the dominant forms, and a pyritohedron. On some crystals the cube had also developed. The crystals in general were tabular in development.

LEAD NITRATE + SUSPENSIONS. The effect of a fine suspension on crystal habit was determined by using magnesium oxide, powdered alundum, powdered kaolinite, and powdered barite. These experiments did not give the results expected. From the results obtained with glycerine it was predicted that a suspension of a fine powder in a solution of either of the nitrates used would have the effect of causing the crystals to become more complex. This, however, was not the case. The crystals produced with lead nitrate at temperatures up to 24°C even at a slow rate of evaporation were all $\pm$ tetrahedrons in combination, equally developed. The tendency is for a smaller number of crystals to form and therefore the crystals produced are larger. The powdered substance was included in all the crystals but was not arranged in any orderly fashion. The distribution was in patches arranged in an irregular manner. No explanation is offered for the results obtained.

DISCUSSION

By way of review it may be mentioned that in general in the study of crystal habit by far the greatest amount of effort seems to have been directed to determine the influence of foreign substances. There seems to have been very little consideration given to control conditions for crystal growth, even to considering the possible influence of such conditions. Very little consideration seems to have been given to the nature of the impurity, to the temperature at which crystal growth takes place and not a great deal to the rate of crystal growth.

The explanations advanced to account for the influence of foreign substances, are based on (1) adsorption, (2) capillarity, and (3) inclusion of the foreign substance into the crystal in a definite manner.

The experiments presented in this paper have been conducted under conditions controlled to a certain extent. The conditions under which the crystals developed were very carefully noted and recorded. The nature of the impurity has been taken into consideration and considerable attention has been given to temperature conditions. An effort has also been made to determine by means of X-ray study, if impurities actually enter into the crystal structure.

There may be cases where adsorption has in some way, not yet fully understood, influenced crystal habit. The results obtained in a large number of experiments point very strongly to the conclusion that this is not always the case. If adsorption were regarded as the cause for the formation of the cube in connection with certain dyes present in a solution of lead nitrate, barium nitrate or strontium nitrate, one would meet with difficulties in explaining results that may be obtained at a temperature of 30°C. If crystals are allowed to grow rapidly at that temperature as has been pointed out, the combination of $\pm$ tetrahedrons results. If the solution while remaining at this same temperature is suddenly transferred to conditions where "slow" crystal growth takes place, pyritohedrons will develop, instead of a cube, in combination with the two tetrahedrons. Furthermore, perfect cubes of each of the three salts studied have been obtained from solutions in which some methylene blue was present, which were entirely free from color.

Also, allowing crystals to grow in the presence of methylene blue at 20°C and then slowly increasing the temperature and finally changing to "slow" rate of evaporation, the crystals will change in

habit from cubes to combinations of cubes and pyritohedrons and also cube, pyritohedrons and $\pm$ tetrahedrons. The fact that crystals may be brought to change in habit in a pure aqueous solution by changing the temperature of crystal growth suggests that the nature of the solvent may have some relation to crystal habit.

Water in an aqueous solution is considered to have different properties than water alone. This has been suggested by the fact that there is a difference in transparency of water in a solution and water in which no substance is dissolved. The modification in crystal habit may possibly be due, in at least some cases, to the nature of the solvent instead of to a peculiar condition existing at the surface of some of the crystal faces by virtue of adsorption of the foreign material. The effect of the nature of the solvent has been clearly demonstrated in some organic compounds, where substances may be produced as needle-like crystals from one solvent and as flaky or tabular crystals from another solvent.

In reviewing further the results obtained with inorganic salts as impurities, it is quite striking that the effect of a foreign substance is intimately related to its solubility. There is sufficient evidence by way of variation in results to suggest that other properties besides the solubility enter into the action to influence crystal habit. The results obtained with ammonium nitrate for instance suggest that viscosity is a property which should be considered.

Also, the salts of elements entering into alkaline and basic compounds (K, Na, Ca, Mg) show a stronger tendency to produce crystals of a simple habit than would naturally be expected by considering their solubilities. Jenkins¹⁴ in considering the velocity of crystallization of urea, acetanilide and ammonium nitrate in various solvents reports that the viscosity of the solution is an important factor.

In considering the effect of inorganic impurities it seems evident that impurities of greater solubility than the salt crystallizing out, increase the rate of crystal growth especially during the first twenty-four hours of crystal development. Ammonium nitrate is known to produce the effect of lowering the viscosity of solutions and the effect of the presence of ammonium nitrate as an impurity to produce simple forms is most marked. In the light of the results reported by Jenkins, it may be concluded that the effect of ammonium nitrate is actually to increase the rate of crystal growth. Hence allowing some for effect of viscosity, it may be regarded, in general,

¹⁴ John D. Jenkins: *J. Am. Chem. Soc.*, **47**, No. 4, April, 1925.

that the effect of inorganic salts is to increase or decrease the rate of crystal growth, depending upon the relative solubility.

The outstanding factors influencing crystal habit seem to be temperature and rate of crystal growth. Of the two, temperature decidedly seems to be the controlling condition. In the light of the theories of Federov, Schönflies and Barlow, partitioning space into space unites or space lattices, or elementary cells which have been substantiated by X-ray studies of crystal structure, it seems quite reasonable to assume that crystal habit is intimately related in some way to crystal structure.

X-RAY PHOTOGRAPHS. It seems reasonable to assume that if foreign substances enter into intimate relation with the atoms or molecules as has been suggested there might be a change in the size of the unit cells, and consequently a change in the space relations of the structure planes. However, a comparison of powder photographs, made by Dr. L. S. Ramsdell of the University of Michigan, showing on the same film diffraction patterns of crystals from pure aqueous solutions and of crystals of the same salt obtained from aqueous solutions containing impurities revealed no difference in structure or in dimensions of the unit cell.

CONCLUSIONS

For every crystalline substance there are possible certain crystal forms. The forms possible may be considered to be determined by the crystal structure. Considering, then, that there is a constant tendency of a crystal surrounded by a liquid medium containing its own substance to reach a state of equilibrium with respect to its immediate surroundings, one particular form may approach a state of equilibrium for a specific condition or set of conditions, more easily than any other form. Several important factors which make up the conditions to which the crystal reacts are: (1) temperature; (2) nature of solvent; (3) presence of foreign particles; (4) viscosity; (5) rate of crystal growth.

When forms are in combination it means the conditions have successively changed, or that the conditions prevailing during the time of crystal growth were not exactly the most favorable for either but a fairly close approach and the forms developed simultaneously, each struggling for existence. If we understood solutions more completely and had a more definite knowledge of the shape of the structural units a more satisfactory explanation of crystal habit might possibly be formulated.

